

PATENT SPECIFICATION

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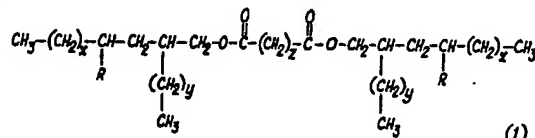


(54) CARBOXYLIC DIESTERS AND THEIR PRODUCTION

(71) We, W. R. GRACE & CO., a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of 1114, Avenue of the Americas, New York, New York 10036, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to esters and their preparation.

The invention provides carboxylic diesters characterised in that they have the general formula



in which;

(a) x is an integer from 1 to 4;

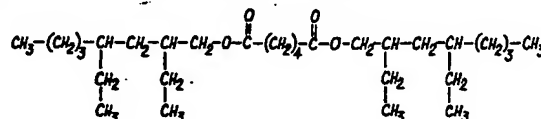
(b) y is an integer from 1 to 4;

(c) R is an alkyl group having 1—4 carbon atoms; and

(d) z is an integer from 1—12 (preferably from 1—9).

Preferred values for x are integers from 1 to 3 (especially 3). Preferred values for y are integers from 1 to 3 (especially 1). R is preferably —CH₂CH₃.

In an especially preferred embodiment of the invention (a) x is 3; (b) y is 1; (c) R is CH₃CH₂; z is 4; and (d) the ester has the formula

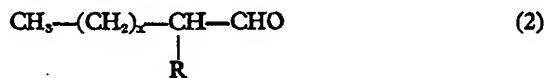


Such esters are useful as base stocks for lubricants. These esters are especially useful as the major component of lubricants for jet engines, reciprocating (piston) engines, and the like, where high or low temperatures are encountered.

The esters of the invention may be prepared by the following sequence of steps:—

Step (a)

By the well-known aldol condensation, two aldehydes are reacted together in the presence of alkali metal hydroxide. The first aldehyde has the formula



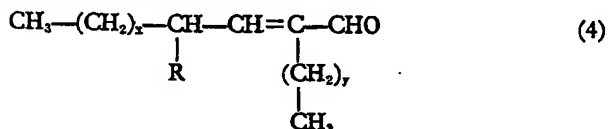
where x is 1, 2, 3 or 4 and R is an alkyl group of 1 to 4 carbon atoms, and the second aldehyde has the formula



where y is 1, 2, 3 or 4.

The aldol condensation using these reactants is effected in a reaction medium comprising an aqueous alkali metal hydroxide solution and a phase transfer catalyst, hereinafter abbreviated to PTC. As is apparent from results given below, use of PTC leads to a much greater yield and much greater conversion of starting material than when the aldol condensation is effected in the absence of PTC.

The resultant aldehydes have the general formula

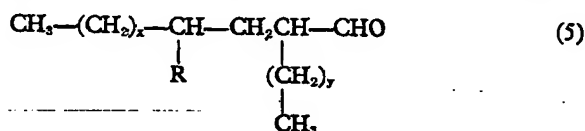


where x, y and R are as defined above.

Preferably x is 3, y is 1 and R is an ethyl group.

10 Step (b)

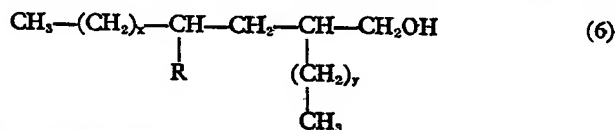
The aldehydes of formula (4) are hydrogenated to saturated aldehydes having the formula



where x, y and R are as defined above.

15 Step (c)

By hydrogenation of the aldehydes of formula (5), or by continued hydrogenation of the aldehydes of formula (4), there can be produced alcohols of formula (6)



where x, y and R are as defined above.

20 Step (d)

These alcohols of formula (6) can be reacted with a dicarboxylic acid having the formula



here z is an integer from 1 to 12, to form an ester having the formula (1).

The invention includes preparation of the esters from the corresponding alcohols by step (d), which may be preceded by step (c) which in turn may be preceded by step (b) and which may be preceded by step (a).

All parts, ratios and percentages in this specification are by weight unless otherwise stated.

Preferred features of the preparation of the aldehyde of formula (4) are:

1. The mole ratio of the first aldehyde to the second aldehyde can be from 20:1 to 1:1 (more preferably 10:1 to 2:1).

2. The temperature of the reaction mixture is adjusted to and maintained at 50—150°C (more preferably 80—100°C).

3. The concentration of the alkali metal hydroxide solution is 4—50% (more preferably 5—15%). Said alkali metal hydroxide solution will usually be KOH, LiOH, or NaOH solution. An amount of alkali metal hydroxide solution effective for promoting aldol addition is used. The amount of alkali metal hydroxide is not critical because a finite amount of said hydroxide solution produces a finite promotion of said aldol addition. We generally use about 1 mole of said alkali metal hydroxide per 10—40 moles of first aldehyde (more preferably 1 mole of said hydroxide per 10—15 moles of said first aldehyde).

4. The exact amount of PTC is not critical. We generally use 1 mole of PTC per 50—200 moles of first aldehyde (preferably about 1 mole of said catalyst per 100 moles of said aldehyde).

5. Contact time ("reaction time") under reaction conditions is not critical and generally varies from 1—2 or 1—3 hours. However, reaction rate is a function of reaction temperature and the longer contact times tend to be required at the lower temperatures recited above while the shorter times tend to be required at the higher temperatures. Thus, for the same conversion (one pass yield), a longer reaction time is required at 50°C than 80°C or 90°C or 125°C.

Typical PTCs which can be used with excellent results in the process of this invention include but are not limited to those listed in Table I, infra.

TABLE I

10	The letters (a) to (d) refer to footnotes below.	10
	Phase Transfer Catalysts (a)	
	Lauryltrimethylammonium chloride	
	Dilauryldimethylammonium chloride	
	Trilaurylmethylammonium chloride	
15	Myristyltrimethylammonium chloride	15
	Dimyristyldimethylammonium chloride	
	Trimyristylmethylammonium chloride	
	Palmityltrimethylammonium chloride	
	Dipalmityldimethylammonium chloride	
20	Tripalmitylmethylammonium chloride	20
	Stearyltrimethylammonium chloride	
	Distearyldimethylammonium chloride	
	Tristearylmethylammonium chloride	
	Oleyltrimethylammonium chloride	
25	Dioleyldimethylammonium chloride	25
	Trioleylmethylammonium chloride	
	(Tall oil) trimethylammonium chloride (b)	
	(Ditall oil) dimethylammonium chloride	
	(Tritall oil) methylammonium chloride	
30	(Tallow) trimethylammonium chloride**	30
	(Ditallow) dimethylammonium chloride	
	(Tritallow) methylammonium chloride	
	Caprylyltrimethylammonium chloride	
	Dicaprylyldimethylammonium chloride	
35	Tricaprylylmethylammonium chloride	35
	(Coco) trimethylammonium chloride (b)	
	(Dicoco) dimethylammonium chloride	
	(Tricoco) methylammonium chloride	
	Dicetyldimethylammonium chloride	
40	Tricetylmethylammonium chloride	40
	Decyltrimethylammonium chloride	
	Didecyldimethylammonium chloride	
	Tridecylmethylammonium chloride	
	Alkyldimethylbenzylammonium chloride (c)	
45	Dialkylmethylbenzylammonium chloride (c)	45
	Laurylmethylethylpropylammonium chloride	
	Laurylethylmethylbutylammonium chloride	
	Tetraurylammonium chloride	
	Dilaurylmethylethylammonium chloride	
50	Dipalmitylethylpropylammonium chloride	50
	Tricaprylylmethylphosphonium chloride	
	Dicaprylylmethylethylphosphonium chloride	
	Caprylylmethylethylpropylphosphonium chloride	
	Stearyldipropylsulfonium chloride	
55	Distearylbutylsulfonium chloride	55
	Tristearylsulfonium chloride	
	Oleyltributylarsonium chloride	
	Dioleyldiethylarsonium chloride	
	Trioleylpropylarsonium chloride	
60	Hexadecyltributyl phosphonium bromide.	60

Footnotes to Table I

(a) while the anion of most of the phase transfer catalysts listed in this table is shown—for convenience in preparing the cable—as chloride, said anion can be

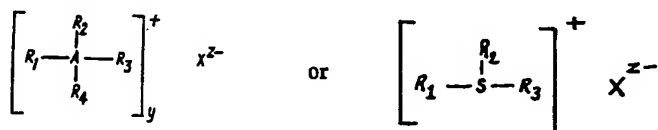
substantially any anion such as bromide, iodine, fluoride, sulfate, phosphate, (hydroxyl) (OH⁻), or the like.

(b) As used herein the term "tall oil" means the mixed alkyl groups obtainable by reducing the fatty acids—predominantly oleic and linoleic acids—(or salts thereof) obtained by saponifying tall oil, "tallow" means the mixed alkyl groups obtainable by reducing fatty acids or salts thereof obtained by saponifying tallow, and "coco" means the mixed alkyl groups obtainable by reducing the fat (or "butter" or grease) obtained from coconuts. See pages 542—557 of Volume 1 of the second Edition of the Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., New York, New York 1963.

(c) As used in these compounds the term "alkyl" means an alkyl group (or a mixture of alkyl groups) each having 7—16 carbon atoms.

(d) "Caprylyl" is the C₈-alkyl group from caprylic acid.

Phase transfer catalysts which can be used with excellent results include but are not limited to those having the formula



in which:

(a) X^{z-} represents an anion (e.g. sulfate, phosphate acetate, nitrate, chloride or bromide);

(b) z is an integer denoting the number of negative charges on each anion;

(c) y is an integer equal to z, so that the cation and anion charges balance;

(d) R₁, R₂, R₃ and R₄ are separately selected from (i) alkyl and alkenyl groups having 1—20 carbon atoms; and (ii) aralkyl groups having 7—16 preferably 7—12 carbon atoms, e.g. benzyl.

(e) A is N, P, or As. It is generally preferred that A be N or P. Preferred PTCs include tricaprylylmethylammonium chloride and didecyldimethylammonium chloride.

In carrying out step (a), we generally prefer to use the following general procedure which we have designated "Procedure A".

Procedure A

A predetermined amount of the first aldehyde is admixed with a predetermined amount of the second aldehyde to form a first admixture.

A predetermined amount of an aqueous solution of an alkali metal hydroxide (preferably NaOH, KOH, or LiOH) containing a predetermined amount of the alkali metal hydroxide is admixed with a predetermined amount of a phase transfer catalyst to form a second admixture. Excellent results can be obtained where using 5—15% NaOH, or KOH solution, or LiOH solution but more dilute and more concentrated alkali solutions can be used without decreasing one-pass-yield or quality of the product aldehyde.

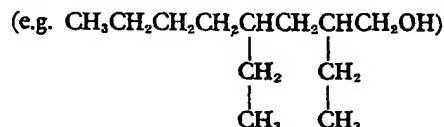
The second admixture is placed in a reaction zone provided with mixing (or The first admixture is added to the second admixture over a predetermined period of time (e.g. 10—80 minutes, or 1—10 hours or 0.5—3 hours depending on the quantities and temperatures involved) while maintaining the temperature of the resulting reacting mixture within a range effective for forming the aldehyde of this invention. Such temperature can be only temperature (or temperature range) from 20 to 150°C and is preferably a temperature (or temperature range) from 60°C to 110°C. If desired, the mixture in the reaction zone can be maintained at such temperature (or within such temperature range) for a period of 15 minutes to 6 hours (or 0.5—1.5 hour) after all of the first admixture has been added to facilitate reaction.

The reacted mixture can be removed from the reaction zone and the product aldehyde recovered therefrom—e.g., by distillation of the reacted mixture using reduced pressure where necessary or desirable to facilitate recovery.

Unreacted starting aldehydes can be recovered and used in a subsequent run. Also side-product aldehydes can be recovered and converted to useful materials. For example, 2-ethylhexenal, which can result from the condensation of 2 molecules of n-butyraldehyde with each other, can be hydrogenated to form 2-ethylhexanal which can be used as first aldehyde in the procedure (Procedure A). Step (b) may be effected by conventional hydrogenation techniques with hydrogen gas using Raney nickel as catalyst, a hydrogen pressure of 200—400 psig and a temperature of

100—200°C. Step (c) may also be effected by conventional hydrogenation techniques with hydrogen gas using nickel, Raney nickel, platinum, or palladium as catalyst. Hydrogen pressures, for example, 400—500 psig at 100—200°C are operable. Step (d), i.e. the esterification reaction, can employ conventional esterification techniques. A preferred procedure is as follows.

Admixing about 2.2 moles of the alcohol of formula (6)



per mole of dioic acid (e.g. azelaic acid), and a suitable catalyst (e.g. p-toluene sulphonic acid) to form a reaction mixture in a reaction zone provided with a heat source, agitating means, an inlet port, an outlet port, and a vent for removing by-product water as water vapour along with vaporized alcohol. It is generally preferred to use 2—2.2 moles of the alcohol per mole of the dioic acid. Unreacted alcohol can be recovered and reused. It is also generally preferred to use 0.2—0.4% (preferably about 0.25%) of the catalyst based on the weight of the dioic acid plus the weight of the alcohol. The thus formed mixture is heated to its reflux temperature and maintained at a temperature effective for removing by-product water until substantially all of the dioic acid has been converted to the ester. Water and excess alcohol which boil off are condensed, and recovered as the reaction progresses. Water, being only slightly soluble in the alcohol can be separated from the recovered alcohol-water mixture. This produces a substantially water-free alcohol which can be recycled to the reaction zone.

Alternatively, toluene can be added to help remove by-product water. If such procedure is used toluene and water boil off. The toluene-water mixture can be condensed and recovered. The toluene can be separated from the water and recycled to the reaction zone. Some alcohol generally vaporizes along with the water and toluene. In such instance a mixture of alcohol and toluene can be separated and recycled. When the esterification has progressed to a predetermined degree, the excess alcohol and any unreacted dioic acid can be separated, and the product ester recovered.

The following Examples illustrate the invention. Examples I to IV illustrate step (a), Example V steps (b), (c) and (d).

EXAMPLE I

Run No. 1, With PTC

A 1 litre flask provided with an agitator means, a reflux condenser, a thermometer, a heating means, and an inlet port was charged with a solution of 33 g water, 14 g sodium hydroxide, and 9.4 g of a PTC (a commercially available tri-carylylmethylammonium chloride).

A "dropping funnel" (additional funnel) was fitted into the inlet port of the 1 litre flask and an admixture of 72 g (1 mole) of n-butyraldehyde and 256 g (2 mole) of 2-ethylhexanal was added, via the dropping funnel, to the mixture in the one litre flask over a period of about 2 1/4 hours while agitating the resulting reacting mixture in said flask and while keeping the temperature of said reacting mixture at about 60°C.

The mixture in the flask was maintained at about 60°C for an hour after all of the admixture of n-butyraldehyde and 2-ethylhexanal had been added. It was then cooled to room temperature.

The cooled mixture was transferred from the 1 litre flask to a separating funnel and separated into an aqueous phase and an organic phase. The organic phase was washed with water until the wash water was neutral to litmus paper. The washed organic phase was dried (with anhydrous calcium sulfate), weighed (309 g), and placed in a container which was labelled "Example I, Product No. 1". The container was closed and set aside for analysis.

Run No. 2, Without PTC

The general procedure of Run No. 1 of this example (Example I) was repeated. However, in this instance the PTC was omitted. The dried organic phase obtained in this run weighed 297 g. It was placed in a container which was labelled "Example I, Product No. 2". The container was then closed to await analysis.

Run No. 3—Analysis of Products Nos. 1 and 2

The above described Products Nos. 1 and 2 prepared in this example were analyzed for product aldehyde (2,4-diethyloctenal, and unreacted reactant aldehydes (n-butyraldehyde and 2-ethylhexanal)) by fractional distillation and gas chromatography of the resulting fractions.

In the case of Product No. 1 (which was prepared with the PTC) it was found that 36% of the 2-ethylhexanal charged had reacted and that 89% of the 2-ethylhexanal which reacted was converted to the desired product aldehyde (2,4-diethyloctenal).

In the case of Product No. 2 (which was prepared without the PTC) it was found that only 20% of the 2-ethylhexanal charged had reacted and that only 45% of the 2-ethylhexanal which reacted was converted to the desired product aldehyde (2,4-diethyloctenal).

EXAMPLE II

Run No. 1, With PTC

This run was made using the apparatus and general procedure used in Run No. 1 of Example I, supra. However, in this instance, reaction temperature was 95°C and the quantities charged were:

Material Charged	Quantity Charged, Moles
Water	7
NaOH	0.2
PTC*	0.02
2-Ethylhexanal	2
n-butyraldehyde	1

*Commercially available tricaprylylmethylammonium chloride.

The admixture of 2-ethylhexanal and n-butyraldehyde was added over a period of 2 hours and the resulting reacting mixture was maintained at 95°C for about an hour after adding the admixture of these aldehydes.

The cooled dried organic phase product was placed in a container labelled "Example 2, Product No. 1", and the container was closed to await analysis of its contents.

Run No. 2, Without PTC

The general procedure of Run No. 1 of this example (Example 2) was repeated. However, in this instance the PTC was omitted.

The cooled dried organic phase product was placed in a container labelled "Example 2, Product No. 2", and the container was closed and set aside for analysis.

Run No. 3—Analysis of Products Nos. 1 and 2

Products Nos. 1 and 2 (from Run Nos. 1 and 2, respectively, of this example (Example 2)) were analyzed according to the general procedure used in Run No. 3 of Example I. It was found that Product No. 1 (from the run using the PTC) contained about 3 times as much of the desired 2,4-diethyloctenal as did Product No. 2 (from the run without the PTC).

EXAMPLE III

The general procedure of Run No. 1 of Example 1 was repeated. However, larger apparatus was used to accommodate larger quantities of materials used in this run. Said quantities were:

Material Charged	Quantity Charged	
	g	Moles
Water	880	49
Sodium Hydroxide	98	2.4
PTC*	66	0.14
n-butyraldehyde	504	7
2-ethylhexanal	1792	14

* The PTC was Aliquat 336 (commercially available tricaprylylmethylammonium chloride).

The dried organic phase product obtained in this run was designated "Example III, Crude Product"; it was analyzed according to the general procedure used in Run No. 3 of Example I.

It was found that 384 g (2.98 moles) of the 2-ethylhexanal had reacted and that 350 g (1.92 moles) of the 2-ethylhexanal had been converted to 2,4-diethyloctenal. In other words, 65.8% of the 2-ethylhexanal which reacted was converted to the desired product (2,4-diethyloctenal).

EXAMPLE IV

This example illustrates step (a) carried out via a batch process in which a lower molecular weight reactant aldehyde, of formula (3), is added over a period of time to an admixture comprising water, alkali metal hydroxide, PTC, and a higher molecular weight reactant aldehyde, of formula (2).

256 g (2 moles) of 2-ethylhexanal, 14 g (0.35 mole) of NaOH, 126 g (7 moles) of water, and 9.4 g (0.02 mole) of a phase transfer catalyst (commercially available tricapyrylmethylammonium chloride) were admixed in a 1 litre flask provided with an agitator means, a reflux condenser, a heating means, and an inlet port having an addition funnel positioned therein. The temperature of the resulting admixture was adjusted to 95°C and 72 g (1 mole) of n-butyraldehyde was added thereto (via the addition funnel) over a period of 5 hours while maintaining the temperature of the material in the flask at about 95°C to form a product mixture.

The product mixture was worked up and analyzed according to the general procedure set forth in Example I, supra. It was found that 25% of the 2-ethylhexanal had reacted, and that 95% of the reacted 2-ethylhexanal had been converted to the desired product, 2,4-diethyloctenal.

Where using the method illustrated by this example we generally add the lower molecular weight reactant aldehyde over a period of 1—6 hours while maintaining the mixture to which said lower molecular weight aldehyde is added at 60—110°C (preferably about 95°C). If desired the reacting mixture can be maintained 60—110°C (preferably about 95°C) for a period of time (e.g., 1/2 to 2 hours) after all of the lower molecular reactant aldehyde has been added. Where using this method it is preferred to use about 1 mole of the lower molecular weight reactant aldehyde per 2 moles of the higher molecular weight reactant aldehyde.

EXAMPLE V

Preparation of 2,4-diethyloctanol and its esters

A 155.4 g portion of an aldehyde fraction boiling at 79—83°C at a pressure of 1 mm of mercury absolute which was obtained by distilling the above described "Example III Crude Product" was analyzed by gas chromatography and found to contain 94.4% of 2,4-diethyloctenal (i.e., it contained 146.6 g of 2,4-diethyloctenal). This material was designated "Reactant 4".

All of Reactant 4 was admixed with hexane (ca. 1000 ml of hexane) and hydrogenated at 140°C under a hydrogen pressure of 440 psig using 1.5 g of Raney nickel as catalyst.

After about 4 hours the hydrogenation was completed. The hexane was then removed from the hydrogenated product by distillation. Analysis of the hydrogenated product showed that it contained 1.25.1 g of 2,4-diethyloctanol which means that 84% of the 2,4-diethyloctenal was converted to 2,4-diethyloctanol.

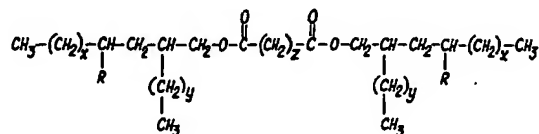
Similar results can be obtained by this procedure in the absence of the hexane which was added as a solvent and diluent because of the small amount of the aldehyde being hydrogenated in a large apparatus.

Esters of 2,4-diethyloctanol can be prepared by the procedure previously described.

The parent application, No. 13483/76 (Serial No. 1,547,856) describes and claims the preparation of an aldehyde from two simpler aldehydes by step (a), which may optionally be followed by step (b), which may optionally then be followed by step (c) to produce alcohols.

WHAT WE CLAIM IS:—

1. Carboxylic diesters having the general formula



where

x is 1, 2, 3 or 4

y is 1, 2, 3 or 4

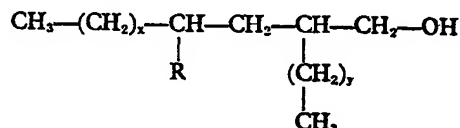
R is an alkyl group having 1 to 4 carbon atoms, and

z is an integer from 1 to 12.

2. Esters according to claim 1 wherein x is 3, y is 1 and R is C₂H₅.

3. Esters according to claim 1 or 2 wherein z is 4.

4. A process of preparing an ester claimed in claim 1, 2 or 3, which comprises reacting an alcohol of formula

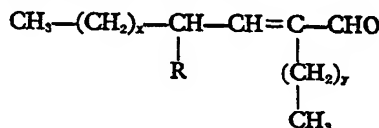


wherein x, y and R are as defined in claim 1, 2 or 3 respectively with an alkanedioxylic acid of formula



where z is as defined in claim 1 or 3 respectively, using at least 2 moles of the alcohol per mole of the acid.

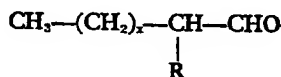
5. A process according to claim 4, which also comprises the preceding step of hydrogenating an unsaturated aldehyde of formula



where x, y and R are as defined in claim 4, or a saturated aldehyde obtained by hydrogenation thereof, until the said alcohol is formed.

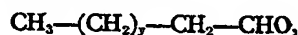
6. A process according to claim 5 which also comprises the preceding step of preparing the said unsaturated aldehyde by the aldol condensation of

(i) a first aldehyde having the formula



wherein x and R are as defined in claim 4, with

(ii) a second aldehyde having the formula



wherein y is as defined in claim 4; in a reaction medium comprising an aqueous alkali metal hydroxide solution and a phase transfer catalyst.

7. A process according to claim 4 substantially as hereinbefore described with reference to any one of Examples I to IV, followed by Example V.

8. An ester according to claim 1 when prepared by a process according to claim 4, 5, 6 or 7.

9. A lubricant containing an ester according to claim 1, 2, 3 or 8 as the base-stock thereof.

J. A. KEMP & CO.
Chartered Patent Agents,
14, South Square,
Gray's Inn,
London, WC1R 5EU.